Hydrochlorination of 6-methoxybenzonorbornadiene[10] in methylene chloride at 0° yielded a 95:5 mixture[11] of 6- and 7-methoxy-*exo*-benzonorbornenyl chlorides.[10] Selective hydrolysis gave 6-methoxy-*exo*-benzonorborneol, converted to the ketone by an Oppenauer oxidation. Addition of the appropriate arylmagnesium bromide yielded the tertiary *endo* alcohols. These were converted to the chlorides which were hydrolyzed to the *exo* alcohols. The alcohols were converted into the *p*-nitrobenzoate and benzoate esters *via* the lithium alkoxides.[5,12]

The esters were subjected to solvolysis in 80% aqueous acetone. The results are summarized in Table I. The data reveal excellent linear correlations with the $\sigma^+$ constants yielding $\rho$ $-3.72$ (correlation coefficient 0.999) for the *exo* series (**1**) and $-4.05$ (correlation coefficient 0.991) for the *endo* series (**2**).

As in the related secondary system,[1] the 6-methoxy substituent exerts little effect on the rates of the 2-aryl-*endo* derivatives. However, in the *exo* series the rate enhancement ($k_{6\text{-OMe}}/k_{6\text{-H}}$) increases from 2.0 for *p*-anisyl, to 4.9 for phenyl, to 34 for *p*-trifluoromethylphenyl, to 40 for *m,m'*-bis(trifluoromethyl)phenyl. This compares with the observed value of 150 for acetolysis of the corresponding secondary brosylates.[1b]

The *endo* derivative has long been utilized as a standard of reference for the rate to be anticipated for the *exo* isomer in the absence of participation. Consequently, we should anticipate that the *exo/endo* rate ratio should increase with increasing electron demand of the 2-aryl group. Indeed, the *exo/endo* rate ratio rises from 7000 for *p*-anisyl, to 14,500 for phenyl, to 25,000 for *p*-trifluoromethylphenyl, to 34,000 for *m,m'*-bis(trifluoromethyl)phenyl.[13]

In the present study the Hammett approach was utilized to maintain the steric effects constant while the electron demand was varied at the 2 position of the benzonorbornenyl system. The results unambiguously confirm the presence of additional $\pi$ participation arising from the presence of the activating methoxy substituent at the 6 position (*homo-para*).

It is important to note that the present approach tests only for the increase in $\pi$ participation attributable to the 6-methoxy substituent over that present in the parent system. (However, the results indicate the absence of significant $\pi$ participation in the parent 2-aryl derivatives[9].) This increase in the *exo/endo* rate ratio in the secondary derivative, × 55, is even less than the *exo/endo* rate ratio in norbornyl itself (× 300), usually attributed to $\sigma$ participation. Yet the same methods applied to 2-norbornyl and 2-camphenilyl fail to reveal any increase whatsoever in the *exo/endo* rate ratio with increasing electron demand by the 2-aryl substituent. We can only conclude that the high *exo/endo* rate and product ratios exhibited by the 2-arylnorbornyl and 2-arylcamphenilyl systems must arise from causes other than $\sigma$ participation.[14]

The importance of $\pi$ participation in the parent 2-arylbenzonorbornen-2-yl system is explored in the following communication.[9]

---

[9] H. C. Brown, S. Ikegami, and K.-T. Liu, *J. Amer. Chem. Soc.*, **91**, 5911 (1969).

[10] Both 6-methoxybenzonorbornadiene and 7-methoxy-*exo*-benzonorbornenyl chloride were kindly made available by Dr. H. Tanida.

[11] Analysis by glpc using a Perkin-Elmer Model No. 226 instrument with 150 ft × 0.01 in. silicone DC 550 column. Previously, the purity was estimated as 97% from solvolytic data.[1d]

[12] All new compounds exhibited sharp melting points, satisfactory elemental analyses, and spectral data consistent with the proposed structure.

[13] Unexpectedly, the 6-methoxy substituent results in an appreciable rate enhancement in the secondary *endo* isomer (× 2.5)[1b] and in the tertiary *endo* isomers containing the more electron-demanding substituents (× 3.7) (Table I). The precise source of this rate enhancement is of considerable interest and we hope to explore its origin. However, its effect is to reduce the observed *exo/endo* rate ratios for both the secondary and the more electron-demanding tertiary derivatives over the values that would have been predicted from the observed rate enhancements in the *exo* isomers.

[14] A detailed pmr study of the 2-phenylnorbornyl cation led the authors to conclude that there is no detectable charge delocalization from the 2 to the neighboring 1 position: D. G. Farnum and G. Mehta, *J. Amer. Chem. Soc.*, **91**, 3256 (1969).

[15] Postdoctorate research associate on a grant (GP 6492 X) supported by the National Science Foundation.

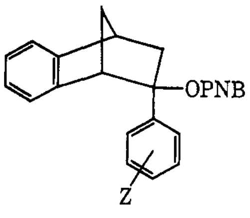
**Herbert C. Brown, Kwang-Ting Liu**[15]
*Richard B. Wetherill Laboratory*
*Purdue University, Lafayette, Indiana 47907*

*Received July 10, 1969*

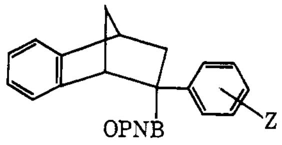
## Solvolysis of 2-Arylbenzonorbornen-2-yl *p*-Nitrobenzoates Containing Representative Substituents in the 2-Aryl Group. Constancy in the *exo/endo* Rate Ratio with Increasing Electron Demand by the 2-Aryl Group

*Sir:*

The *exo/endo* rate ratio in the solvolysis of the 2-arylbenzonorbornen-2-yl *p*-nitrobenzoates (**1**, **2**) remains sensibly constant at ~3000 as the electron demand of the 2-aryl substituent is varied over a major range in reactivity (>$10^8$). This observation indicates the absence of $\pi$ participation as a significant factor in the high *exo/endo* rate ratio (~3000) observed in these 2-arylbenzonorbornen-2-yl derivatives.



1



2

The near-constancy of the *exo/endo* rate ratios in the benzonorbornen-2-yl derivatives (2-H, 15,000; 2-Me, 6500; 2-Ph, 2900) originally led to the conclusion that $\pi$ participation could not be a major factor in these high rate ratios.[1] It has long been accepted that participation by a neighboring group should decrease with increasing stability of the electron-deficient center.[2,3] The observation that a 6-methoxy group enhanced the *exo/endo* rate ratio by a factor of 55[4] was not inconsistent with this conclusion. However, the observation that a nitro group at the 6 or 7 position decreased the *exo/endo* rate ratio to approximately 100[4d] did appear to

---

[1] H. C. Brown and G. L. Tritle, *J. Amer. Chem. Soc.*, **88**, 1320 (1966). The values are slightly modified from those originally used to take advantage of later, more precise measurements.

[2] S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *ibid.*, 74, 1113 (1952).

[3] For example, the rate factor of $10^{11}$ for the participation in *anti*-7-norbornenyl is decreased drastically to a factor of less than $10^2$ by a 7-phenyl substituent: P. G. Gassman and A. F. Fentiman, Jr., *ibid.*, **91**, 1545 (1969).

[4] (a) P. D. Bartlett and W. P. Giddings, *ibid.*, **82**, 1240 (1960); (b) D. V. Braddon, G. A. Wiley, J. Dirlam, and S. Winstein, *ibid.*, **90**, 1901 (1968); (c) H. Tanida, H. Ishitobi, and T. Irie, *ibid.*, 90, 2688 (1968); (d) H. C. Brown and G. L. Tritle, *ibid.*, **90**, 2689 (1968).

Table I. Rates of Solvolysis of 2-Arylbenzonorbornen-2-yl *p*-Nitrobenzoates in 80% Aqueous Acetone

| | | | | | | Relative rates at 25° | | | |
|---|---|---|---|---|---|---|---|---|---|
| Substituent in 2-aryl | Isomer (OPNB) | Temp, °C | $10^6 k_1$,[a] $\sec^{-1}$ | $\Delta H^{\ddagger}$, kcal/mol | $\Delta S^{\ddagger}$, eu | *exo* | *endo* | *exo*/*endo* 6-H | *exo*/*endo*[b] 6-MeO |
| *p*-$OCH_3$ | *exo*[c] | 25.0 | 1080[c] | | | 4000 | | 3300 | 7,000 |
| | *endo*[f] | 75.0 | 144 | | | | | | |
| | | 50.0 | 8.69 | | | | | | |
| | | 25.0 | 0.328[c] | 24.5 | −6.0 | | 3300 | | |
| *p*-H | *exo*[h] | 75.0 | 111 | | | | | | |
| | | 50.0 | 7.0 | | | | | | |
| | | 25.0 | 0.278[e,g] | 24.1 | −7.7 | 1.00 | | 2900 | 14,500 |
| | *endo*[h] | 125.0 | 24.6 | | | | | | |
| | | 100.0 | 2.05 | | | | | | |
| | | 25.0 | $9.71 \times 10^{-5}$[e] | 28.8 | −8.0 | | 1.00 | | |
| *p*-$CF_3$ | *exo*[i] | 125.0 | 93.4 | | | | | | |
| | | 100.0 | 8.16 | | | | | | |
| | | 25.0 | $4.67 \times 10^{-4}$[e] | 28.2 | −6.6 | 0.0017 | | 2700 | 25,000 |
| | *endo*[j] | 150.0 | 3.21 | | | | | | |
| | | 125.0 | 0.262 | | | | | | |
| | | 25.0 | $1.72 \times 10^{-7}$[e] | 33.0 | −6.3 | | 0.0018 | | |
| *m,m'*-$(CF_3)_2$ | *exo*[k] | 150.0 | 29.8 | | | | | | |
| | | 125.0 | 3.07 | | | | | | |
| | | 25.0 | $7.73 \times 10^{-6}$[e] | 29.8 | −9.3 | $2.8 \times 10^{-5}$ | | (2800) | (34,000) |
| | *endo* | 25.0 | $2.8 \times 10^{-9}$[l] | | | | $(2.9 \times 10^{-5})$ | | |

[a] Computer calculated using least-squares program. [b] Reference 7. [c] This ester was so unstable that purification failed. The rate was measured in the impure state. However, the rate ratio, $k_{OPNB}/k_{OBz}$, 20.5, is very close to 20.8 observed in the solvolysis of 2-*p*-anisyl-*exo*-2-norbornyl esters; footnote *d*. Benzoate, mp 129–129.5°, $k_1^{25}$ $5.28 \times 10^{-5}$ $\sec^{-1}$. [d] H. C. Brown and K. Takeuchi, *J. Amer. Chem. Soc.*, **90**, 2691 (1968). [e] Calculated from data at other temperature. [f] Decomposed at 130°. [g] The rate constant was reported as $0.305 \times 10^{-6}$ $\sec^{-1}$ based on the data at 100° and at 75°. [h] Reference 1. [i] Mp 147.0–147.5°. [j] Mp 165–166.5°. [k] Mp 214–215° dec. [l] Estimated by extrapolation of the log $k$–$\sigma^+$ plot for other derivatives.

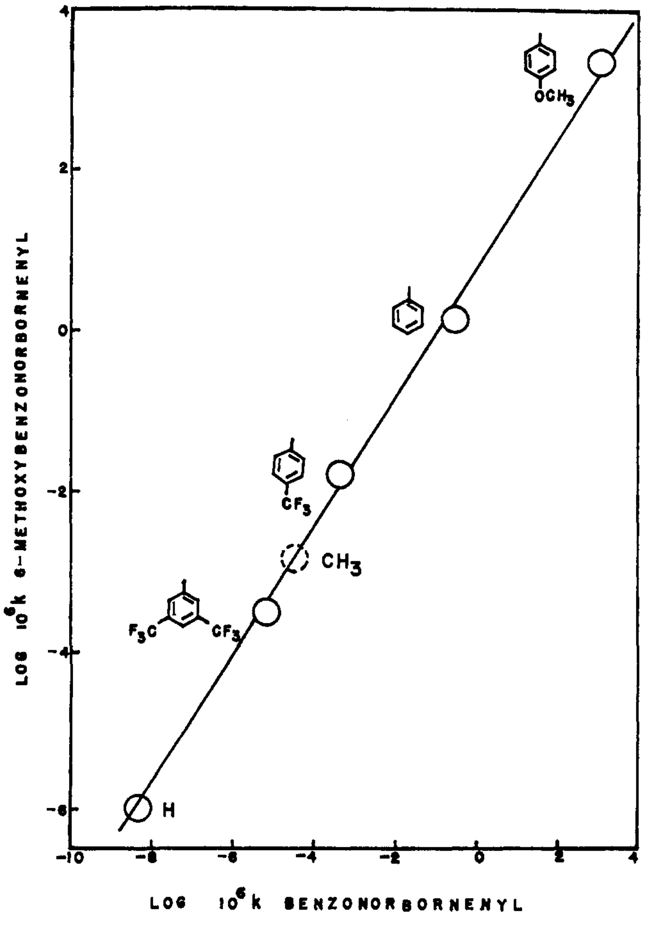


Figure 1. Correlation of the rates of the 2-substituted *exo*-benzonorbornenyl *p*-nitrobenzoates with the rates of the 2-substituted 6-methoxy-*exo*-benzonorbornenyl *p*-nitrobenzoates at 25°. (The line is defined by the 2-aryl points only.)

be inconsistent with the earlier conclusion and encouraged us to undertake more extensive studies in the hope of resolving the inconsistencies.[5]

The Hammett approach permits one to vary the electron demand at a carbonium ion center over a wide range while maintaining the steric effects essentially constant.[3,6] Application of this technique to 2-aryl-6-methoxybenzonorbornen-2-yl derivatives revealed a regular increase in the *exo*/*endo* ratio with increasing electron demand of the 2-aryl substituent.[7] Accordingly, it appeared appropriate to apply this technique to the parent system to test for the importance of $\pi$ participation in the high *exo*/*endo* rate ratio observed for the 2-phenyl derivative.

The 2-aryl-*endo*-benzonorbornenols were synthesized by addition of the appropriate arylmagnesium bromide to the ketone. Conversion of the alcohols to the chlorides followed by hydrolysis yielded the *exo* isomers. These were converted into the esters in the usual manner.[7,8] The compounds were solvolyzed in 80% aqueous acetone. The results are summarized in Table I.

The data reveal excellent linear correlations with the $\sigma^+$ constants, with a $\rho$ of −4.50 (correlation coefficient

---

(5) A detailed study of secondary benzonorbornen-2-yl derivatives containing deactivating substituents in the aromatic ring was described by H. Tanida at the Conference on Carbonium Ions, Cleveland, Ohio, Oct 1968. It is beginning to appear that major anomalies in the data involving acetolysis of secondary alkyl arenesulfonates may arise from a need to revise the original conclusion that such solvolyses approach the limiting category in character (S. Winstein, E. Grunwald, and H. W. Jones, *J. Amer. Chem. Soc.*, **73**, 2700 (1951)). See P. von R. Schleyer and C. J. Lancelot, *ibid.*, **91**, 4297 (1969), for a discussion of the problem with pertinent literature references.

(6) H. C. Brown and K. Takeuchi, *ibid.*, **90**, 2691, 2693, 5268, 5270 (1968).

(7) H. C. Brown and K.-T. Liu, *ibid.*, **91**, 5909 (1969).

(8) All new compounds exhibited sharp melting points, satisfactory elemental analyses, and spectral data consistent with the proposed structure.

1.000) for the *exo* series **1** and −4.52 (correlation coefficient 1.000) for the *endo* series **2**.

In contrast to the 6-methoxy derivatives,[7] the *exo/endo* rate ratios are essentially constant, exhibiting values of 3300 for *p*-anisyl, 2900 for phenyl, 2700 for *p*-trifluoromethylphenyl, and 2800 for *m,m'*-bis(trifluoromethyl)phenyl.

In both the *exo* series and the *endo* series the rates at 25° vary over a range of approximately $10^8$. This represents an enormous range of electron demand by the carbonium ion center. If the original postulate that participation should increase with increasing electron demand[2] is valid, there does not appear to be any reasonable way to avoid the conclusion that $\pi$ participation cannot be a major factor in these tertiary 2-arylbenzonorbornen-2-yl derivatives.

If $\pi$ participation is not a major factor in the high *exo/endo* rate ratio observed for these derivatives, what can be the cause?

The ground-state energies of a 2-aryl and 2-*p*-nitrobenzoate substituent appear to be very similar.[9] Consequently, differences in ground-state energies cannot be a significant factor.

We appear to be forced to steric hindrance to ionization in the *endo* isomer as the explanation for the high *exo/endo* rate ratios in these tertiary systems.[10]

The apparent absence of $\pi$ participation in these tertiary derivatives does not rule out the possibility that $\pi$ participation may be a factor in the *exo/endo* rate ratio for the secondary isomer. This could account for the effect of the (6,7)-nitro substituent in greatly decreasing the *exo/endo* rate ratio of the parent secondary system. Unfortunately, this problem has now become involved in the more general question as to the precise nature of the solvolysis process for secondary alkyl arenesulfonates and may well require a resolution of that question before a satisfactory understanding of the behavior of the secondary derivatives is attained.

We are further testing the validity of the present interpretation by examining the *exo/endo* rate ratios in 2-arylbenzonorbornen-2-yl derivatives containing deactivating substituents in the benzo moiety.

Since the present results indicate that the 2-aryl-*exo*-norbornenyl derivatives are not influenced significantly by $\pi$ participation, it is of interest to use these compounds as standards against which the rate accelerations produced by a 6-methoxy substituent can be measured. As pointed out earlier, the rate acceleration, as measured by the value of $k_{6\text{-OMe}}/k_{6\text{-H}}$, increases with increasing electron demand: 2.0 for *p*-anisyl, 4.9 for phenyl, 34 for *p*-trifluoromethylphenyl, and 40 for *m,m'*-bis(trifluoromethyl)phenyl.[7]

Indeed, the rate constants for the 6-methoxy tertiary derivatives plot linearly against the rate constants for the corresponding unsubstituted benzo derivatives (Figure 1). Surprisingly, the line defined by the tertiary *p*-nitrobenzoates correlates quite well the calculated rate constants for the corresponding secondary *p*-nitrobenzoates.[11] If the 2-methyl derivatives also obey this correlation, a rate enhancement of 39 at 25° would be predicted for 6-methoxy-2-methyl-*exo*-benzonorbornenyl *p*-nitrobenzoate.

The present data for the tertiary derivatives argue strongly for the absence of significant $\pi$ participation in the 2-arylbenzonorbornen-2-yl derivatives. The observation that the data for the secondary derivatives are correlated so well with the data for the tertiary derivatives suggests that $\pi$ participation may not be a major factor even in the parent secondary benzonorbornen-2-yl system. However, it is necessary to understand the large effect of the (6,7)-nitro substituent on the *exo/endo* rate ratio before a final decision can be reached.

---

(9) M.-H. Rei and H. C. Brown, *J. Amer. Chem. Soc.*, **88**, 5335 (1966); M.-H. Rei, Ph.D. Thesis, Purdue University, Lafayette, Ind., 1967.

(10) H. C. Brown and W. J. Hammar, *J. Amer. Chem. Soc.*, **89**, 6378 (1967); H. C. Brown, I. Rothberg, and D. L. VanderJagt, *ibid.*, **89**, 6380 (1967); H. C. Brown, W. J. Hammar, J. H. Kawakami, I. Rothberg, and D. L. VanderJagt, *ibid.*, **89**, 6381 (1967).

(11) These were calculated using a factor of 3 × $10^5$ to estimate the rates of the *p*-nitrobenzoates from those of the chlorides.[4d]

(12) Postdoctorate research associate on a grant (GP 6492 X) supported by the National Science Foundation.

**Herbert C. Brown, Shiro Ikegami,[12] Kwang-Ting Liu[12]**
*Richard B. Wetherill Laboratory*
*Purdue University, Lafayette, Indiana 47907*

*Received July 10, 1969*

---

## Relative Basicity of Phosphine and Ammonia in the Gas Phase[1]

*Sir:*

Phosphine in aqueous solution has been estimated[2a] to be 17–23 p*K* units less basic than its congener ammonia. Differences in energies of solvation, rehybridization, electronegativity, and possibly nonbonded repulsions may all play a role in influencing the relative basicities.[2] A quantitative gas-phase determination of the basicities (proton affinities) of $PH_3$ and $NH_3$ is desirable to estimate the relative importance of the above factors.

The proton affinity (PA) of a species, M, is the negative of the enthalpy change for the process $M + H^+ \rightarrow MH^+$. Recently, Haney and Franklin[3] have reported a value of 207 kcal/mol for the proton affinity of $NH_3$. The proton affinity of $PH_3$ is less well known. Previous estimates[4–7] for its value range from 153 to 209 kcal/mol. Clearly, new and more reliable data are desirable. Consider the general gas-phase proton-transfer reaction of eq 1. Ion–molecule reactions

$$\mathrm{M_1 + M_2H^+ \rightleftarrows M_1H^+ + M_2} \qquad (1)$$

proceed with negligible activation energy.[8] Thus reaction 1 will proceed to the right *only if* $PA(M_1) \geq PA(M_2)$.[9] We have derived the proton affinity of phosphine by determining the course of reaction 1 in mixtures of phosphine with compounds of known proton affinity.

---

(1) This research was supported by the U. S. Atomic Energy Commission under Grant AT(04-3)767-8.

(2) (a) R. F. Hudson, "Structure and Mechanism in Organo-Phosphorus Chemistry," Academic Press, New York, N. Y., 1965, p 16; (b) E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 304–308, 315–322 (1963).

(3) M. A. Haney and J. L. Franklin, *J. Chem. Phys.*, **50**, 2028 (1969). In agreement with these authors, we have recently obtained a value of PA($NH_3$) = 207 ± 3 kcal/mol employing procedures similar to those described in the present communication: J. L. Beauchamp and W. T. Huntress, unpublished results.

(4) W. Wendlandt, *Science*, **122**, 831 (1955).

(5) A. Giardini-Guidoni and G. G. Volpi, *Nuovo Cimento*, **17**, 924 (1960).

(6) Y. Wada and R. W. Kiser, *J. Phys. Chem.*, **68**, 2294 (1964).

(7) T. C. Waddington, *Trans. Faraday Soc.*, **61**, 2652 (1965).

(8) F. W. Lampe, J. L. Franklin, and F. H. Field, *Progr. Reaction Kinetics*, **1**, 67 (1961).

(9) J. L. Beauchamp and S. E. Buttrill, Jr., *J. Chem. Phys.*, **48**, 1783 (1968). The instrumentation and techniques employed are described herein.